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Discrimination of mango fruit maturity by volatiles using the electronic nose and gas chromatography☆

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Abstract

Mango fruit (*Mangifera indica* L.), cv. 'Cogshall', 'Kent' and 'Keitt' were harvested at different maturities (61–115 d past flowering and 80–307 average g fresh weight for 'Cogshall') and at different sizes (364–1563 and 276–894 average g fresh weight for 'Keitt' and 'Kent', respectively). Immediately after harvest (green) or after 1 week of ripening at room temperature (ripe), fruit were homogenized or left intact and evaluated by electronic nose (enose) or by gas chromatography (GC) for aroma and other volatiles as well as for soluble solids and acids. Volatile data from the different harvest maturities and ripening stages were discriminated by using multivariate statistics (discriminant factor analysis). Both the enose and GC were able, in most cases, to separate fruit from different harvest maturities, especially for 'Cogshall' mangoes, at both the green and ripe stages as well as discriminate green from ripe fruit and fruit from the different varieties within a maturity stage. Solids and acids data indicated that later harvest maturities resulted in sweeter fruit and later-harvested fruit had a different volatile profile from earlier-harvested fruit. Mango fruit volatiles may be useful as maturity markers to determine optimal harvest maturity for mango fruit that results in full quality upon ripening.
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Keywords: Mango; Electronic nose; Aroma volatiles; Harvest maturity

1. Introduction

Mango fruit, *Manguifera indica* L. originated in Burma and India and are grown in most tropical regions of the world. There are 49 species and thousands of cultivars. Mango fruit are climacteric (Pantastico, 1984) and mature between the eleventh and fourteenth week after fruit set. Disorders are observed when fruit are harvested too early (Sy et al., 1989), yet the appropriate harvest maturity stage for optimal postharvest quality is difficult to determine, and varies by cultivar. Normally, fruit are harvested at the not clearly defined "mature green" stage for export markets, but subsequently ripen with poor quality if harvested immature. Biochemical measurements that are used as a maturity index for other fruit crops include titratable acidity, total soluble sugars, starch content, carotenoids, and physical measurements such as fruit weight, firmness and color, but are not always correlated with optimal quality (Cristo, 1994), and often require destruction of the fruit. One report successfully used dry matter and starch to predict soluble solids content using near infared spectroscopy (Saranwong et al., 2004) as an indication of quality. Nevertheless, other methods of measuring maturity for optimal postharvest flavor quality are still needed, especially if non-destructive.

Mango is a climacteric fruit, and as such, important biochemical changes occur during the respiratory climacteric, just before ripening. Most volatile compounds, such as terpene alcohols, nor-isoprenoid derivatives, and aromatic alcohols are glycosidically bound, and are liberated during ripening (Sakho et al., 1985). Harvest maturity can affect this process and affect the final flavor/aroma quality of the ripened fruit (Bender et al., 2000).

A review of the publications identifying volatile compounds in mango fruit reported a total of 267–435 compounds (Maarse,

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1991; Nijssen et al., 1999). Terpene hydrocarbons are the major class of compounds in mango, with contents of 16–90%. δ-3-Carene is the major compound in most mango cultivars, with limonene, β-ocimene, myrcene and α-terpinolene having importance in some cultivars. δ-3-Carene is believed to be the compound responsible for the typical mango aroma (MacLeod and Pieris, 1984; MacLeod and Snyder, 1985), and sesquiterpene hydrocarbons may also be in amounts as high as 10% in some cultivars, with large variability between cultivars (Sakho et al., 1985). Oxygenated compounds vary among mango varieties including alcohols, ketones, and esters. Along with the terpene and sesquiterpene hydrocarbons, they all contribute to the characteristic mango flavor.

Volatile (often aroma) compounds are traditionally analyzed by gas chromatography (GC) analysis with flame ionization (FID) or mass spectrophotometer (MS) detectors. Headspace sampling allows identification of aroma volatiles in the vapor phase in equilibrium with the solid or liquid sample matrix (Bicchi and Joulain, 1990). The static headspace technique is easy to implement, but has its limitations due to the low concentration of volatiles in the headspace, and small volumes that one can inject in a GC and be detected by an FID or MS detector. Another detection system coupled to headspace sampling is the electronic nose (enose). The use and optimization of an enose with fruit has been studied on orange juice (Shaw et al., 2000), tomato by Maul et al. (1997, 1998, 2000), and on apples (Bai et al., 2004). While many industries rely on the classical analytical techniques of gas or liquid chromatography, or on sensory analyses to evaluate product flavor and aroma, enose allows differentiation between products based on the volatile compounds.

In this study, volatile compounds were investigated in the context of finding new maturity markers for mango (Ackerman and Torline, 1984) in whole mango fruit and fruit homogenate in a joint project with the French Agricultural Research Center for Agricultural Development (CIRAD) and the USDA/ARS Citrus and Subtropical Products Laboratory (USCSPL) using enose and GC. In addition, harvest maturity was investigated for effect on mango flavor compounds.

2. Materials and methods

2.1. Fruit material

Reunion Island mangoes, cv. Cogshall, were harvested from a commercial orchard every 7–14 d from fruit set to commercial maturity (61–115 d after fruit set, mature green stage, Table 1), and were air-shipped to Marseille, France and transported to CIRAD, Montpellier, France. One batch of four fruit was immediately homogenized individually upon receipt (green fruit), while the remaining 6–8 fruit were ripened in air at 20 °C for 1 week prior to homogenizing (ripe fruit). Each homogenized fruit was frozen individually, stored at −20 °C, and was considered a single sample unit for later electronic nose or gas chromatography (GC) analysis, both of which were performed in duplicate.

Florida mangoes, cvs. Keitt and Kent, were harvested at different sizes from a commercial grove in Homestead, FL, transported to the USCSPL and sorted by weight into five lots of 6–18 fruit/lot, ranging from 364 to 1563 g for 'Keitt', and 10–23 fruit, ranging from 276 to 894 g for 'Kent', to get a range of harvest maturities. After ripening, 'Keitt' and 'Kent' fruit from each lot were divided into three replicates of 2–7 fruit each and homogenized after ripening for GC analysis.

2.2. Gas chromatography

For 'Cogshall' mango, volatile analysis was performed at CIRAD in France. A sampling flask containing 2 g mango homogenate was diluted with 20 mL distilled water, and placed in a water bath at 37 °C. Helium was swept through the homogenate at 20 mL/min, and adsorbed on a trap made of a mixture of activated charcoal and graphite, for 1 h at 37 °C. Desorption was by a MW-1 microwave sampler (Rektorik, 1982). The trap was subjected to microwaves for 7 s, allowing for a split 1:20 flash injection. Compound separation was on a Varian 3400 GC equipped with a Flame Ionization detector (FID) and using a DB-Wax column (60 m, 0.32 mm i.d., 0.25 μm film thickness, J&W Scientific, Folsom, CA). Injector and detector temperatures were 190 and 230 °C, respectively. The temperature program was 50 °C for 6 m, increased to 220 °C at 6 °C m^{-1}, then held for 16 m. Compounds were identified by transferring the portable microwave unit onto a GC 8000 FISON (Thermo Separation Products) equipped with a quadrupole TRIO 1000 FISON MS. Mass spectra data acquisition conditions were: positive electron impact, 35–400 *m/z*, 70 eV, transfer temperature 190 °C, source temperature 180 °C, electron multiplier detector at 500 V. Data are shown as intensity of GC detector signal (mV).

For 'Keitt' and 'Kent' mango, volatile analysis was performed at the USCSPL in Florida. Homogenate, diluted 50% with deionized water (v/v) (2 mL), was placed in a 6 mL sealed vial and fast frozen by immersion in liquid nitrogen and stored at −20 °C until analysis. The vial was equilibrated at 80 °C for 15 m in a static headspace sampler (Perkin-Elmer HS6, Boston, MA) coupled to a Perkin-Elmer 8500 GC equipped with a FID. The column used was a DBWAX (J&W Scientific, Folsum, CA) with a polar coating (30 m, 0.53 mm i.d., 1 μm film thickness). Carrier gas was He at 56 cm s^{-1}. The temperature was held at 40 °C for 6 m then increased to 180 °C at 6 °C m^{-1}. Compound identification was by retention time comparison to known standards as well as by spiking deodorized homogenate with five levels of known compounds to form calibration curves (Malundo et al., 1997). Compound identities were confirmed by analyzing samples from the same fruit by GC/MS. In this case, mango homogenate, 600 mL, was diluted with 600 mL DI water and then centrifuged at 6000 × *g* for 15 m. Organic compounds were extracted from the supernatant using methylene chloride and examined using a GC–MS (MSD 5973, Agilent, Palo Alto, CA), fitted with a DB5 column (30 m, 0.32 mm i.d, 1 μm film thickness, J&W Scientific) (Malundo et al., 1997; Lebrun et al., 2004).

2.3. Electronic nose

2.3.1. Fruit pulp

The enose FOX 4000 (Alpha MOS, Toulouse, France) was equipped with an automatic headspace sampler HS100 (Alpha

Table 1
Weight of 'Cogshall' mango fruit harvested at different maturities for green fruit (after harvest) and ripe fruit (1 week after harvest)

Maturity (days past flowering)	Green		Ripe	
	No. of fruit	Weight (g)	No. of fruit	Weight (g)
61	4	79.6 ± 10.9	6	90.1 ± 30.3
75	4	126.7 ± 17.3	8	126.9 ± 32.7
103	4	249.1 ± 18.7	4	239.6 ± 10.6
115	4	275.3 ± 26.7	8	306.7 ± 20.3

MOS) and with 18 metallic oxide sensors (coated and uncoated). Mangoes were analyzed as homogenates, or whole fruit. Thawed mango homogenate was diluted with deionized (DI) water to 25% of original homogenate (v/v, homogenate/water) (Lebrun et al., 2004) and homogenized in a Waring blender (Waring Products Corp., New York) at 27,000 × *g* for 40 s. Homogenate (2 mL) was placed in a 10-mL vial and allowed to equilibrate for 1 h at 10 °C on the HS 100 headspace sampler. The samples were heated to 50 °C and shaken for 3 m just before headspace sampling. Headspace (500 μL) was injected at 2000 μL s^{-1}, and signal acquisition lasted 2 m, followed by 8 m for baseline recovery. Each injection was repeated six times per sample.

2.3.2. Intact fruit

Intact mangoes, of similar color, were sorted by weight into five lots (6–18 fruit/lot, ranging from 364 to 1563 g for 'Keitt', and 10–23 fruit, ranging from 276 to 894 g for 'Kent') and placed in sealed plastic containers (18.9 L). Sorting by weight was performed based on the principle that larger fruit were riper than smaller fruit for that specific year, because bloom had been very synchronized that season, and as was observed for weight range versus days past fruit set for 'Cogshall' mangoes, which although smaller, increased over threefold in weight from early to later harvest maturity (Table 1) as did 'Keitt' and 'Kent'. Container lids, fitted with a rubber gasket, were equipped with septa for headspace sampling, and with a flexible balloon to equilibrate the internal pressure during headspace sampling. Fruit were held at 28 °C for 3 h, then 30 mL of headspace were withdrawn from the container. The headspace sample was injected into a 10-mL sampling vial equipped with a venting tube for flushing several times the vial volume with sample (venting tube was removed after flushing). The sampling vials were equilibrated for 1 h at room temperature on the HS100 autosampler (Alpha MOS, Toulouse, France). The vials were then heated to 40 °C for 60 s, and 2000 μL of vial atmosphere were injected in quadruplicate into the electronic nose at 2000 μL s^{-1} (Lebrun et al., 2004). All headspace injections were followed by a blank injection of the headspace of an empty container sealed for the same amount of time as for the fruit samples to account for any volatiles produced by the container itself or room air. Since this method did not result in volatile concentrations that could be observed by headspace GC, the fruit were combined into six replicates/lot, homogenized and then analyzed by GC as described earlier.

2.4. Biochemical measurements

'Cogshall' mango homogenates were analyzed for total soluble solids (TSS) using a refractometer with temperature correction (ATAGO U.S.A., Inc., Bellevue, WA), and for titratable acidity (TA) and pH using a pH-meter (JENCO model 6071, JENCO, SanDiego, CA). For TA, mango homogenates (10 g) were manually titrated to pH 8.1 with 0.1N NaOH.

2.5. Statistical analyses

Analysis of variance was performed for volatile data obtained by GC and for biochemical data using the SAS software (SAS, 1999). Separation of means was performed with the LSD test ($\alpha = 0.05$). Data from the electronic nose were analyzed using discriminant factor analysis (DFA). The Prometheus software (Alpha MOS) was used for sensor optimization when appropriate and for data analysis. Prediction interval ellipses around observations within a group show the prediction interval for differences from other observations at 95% confidence level.

Table 2
'Cogshall' mango fruit pH, titratable acidity (TA) and total soluble solids (TSS) at different maturities immediately after harvest (green) and after 1 week of ripening at 20 °C (ripe)[a]

Harvest maturity (days after fruit set)	pH		TA (g L^{-1})		TSS (%)	
	Green	Ripe	Green	Ripe	Green	Ripe
61	3.30 bc B	3.70 a A	4.02 a A	1.80 a B	7.55 b B	9.80 b A
75	3.22 c B	3.65 a A	3.98 a A	2.18 a B	6.85 b B	9.32 b A
103	3.31 b B	3.53 a A	3.65 a A	1.58 a B	9.05 a B	14.67 a A
115	3.41 a A	3.60 a A	3.86 a A	1.77 a B	7.50 b B	14.22 a A

[a] Data are means of four to eight fruits, and means followed by a different lower case letter within a column, and means between "green" and "ripe" fruit within a harvest date followed by a different upper case letter are statistically different by the LSD test ($\alpha = 0.05$).

3. Results and discussion

3.1. Solids and acids for 'Cogshall' mangoes

3.1.1. Comparison of green and ripe fruit

Mangoes are usually harvested in a mature but unripe stage 75–135 d past blooming, depending on cultivar, weather and cultivation practices (Narain et al., 1998). 'Cogshall' fruit were analyzed immediately after harvest (green) and after ripening (ripe). For green versus ripe fruit within each harvest maturity (61–115 d after fruit set), pH and TSS increased and TA decreased as the fruit ripened for all harvest maturities, except for pH of the last harvest date that was not significant (Table 2). These data indicate that the fruit ripened as evidenced by decreasing acids and increasing solids for all harvest maturities, which is typical for mango (Mitra and Baldwin, 1997).

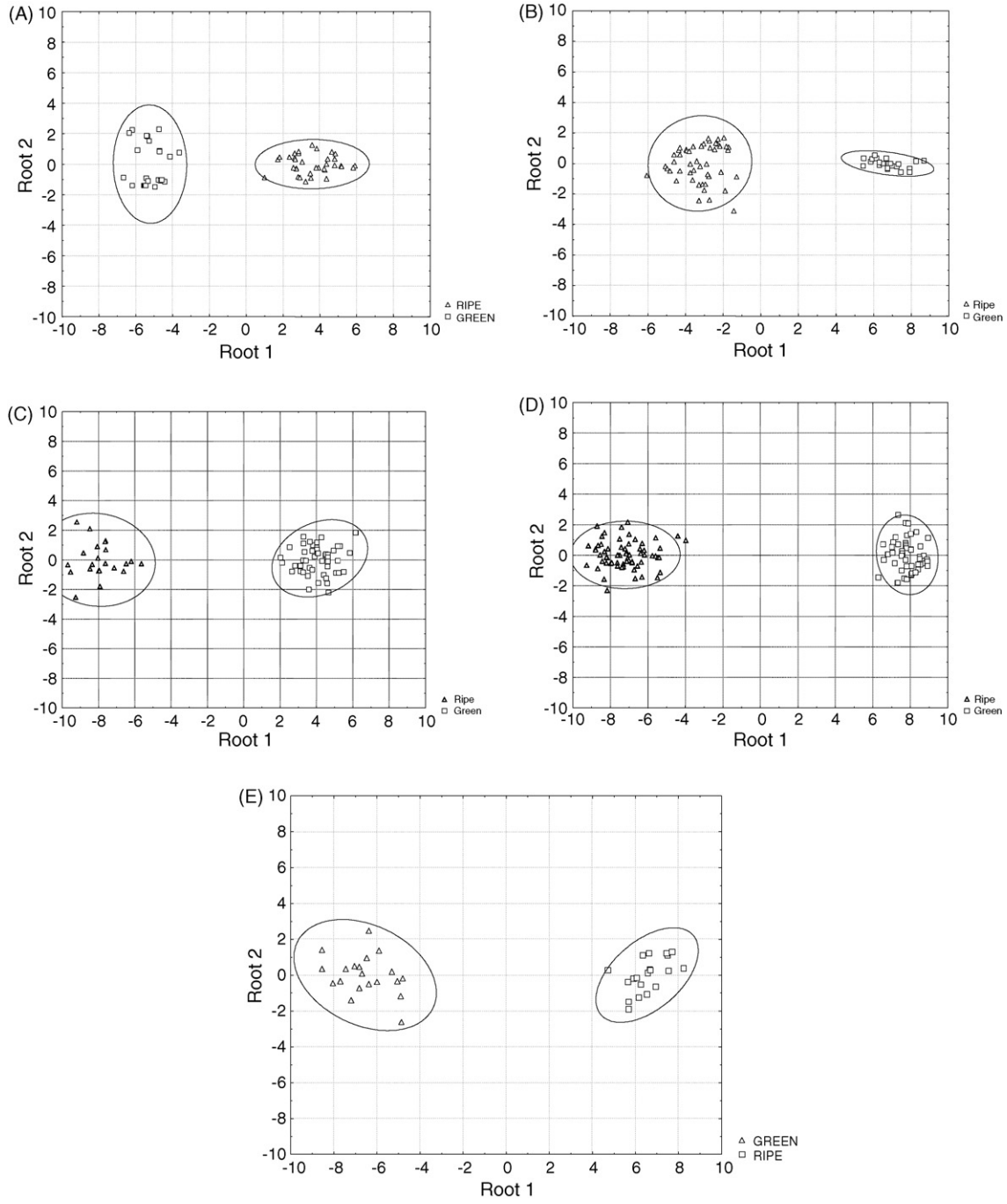

Fig. 1. Comparison between green and ripe 'Cogshall' mangoes by enose using discriminant factor analysis of homogenate for fruit harvested (A) 61 d, (B) 75 d, (C) 103 d, and (D) 115 d passed flowering, immediately after harvest (green), after 1 week of ripening (ripe); and (E) 'Keitt' mango immediately after harvest at full-sized mature green (green) and after 1 week of ripening (ripe).

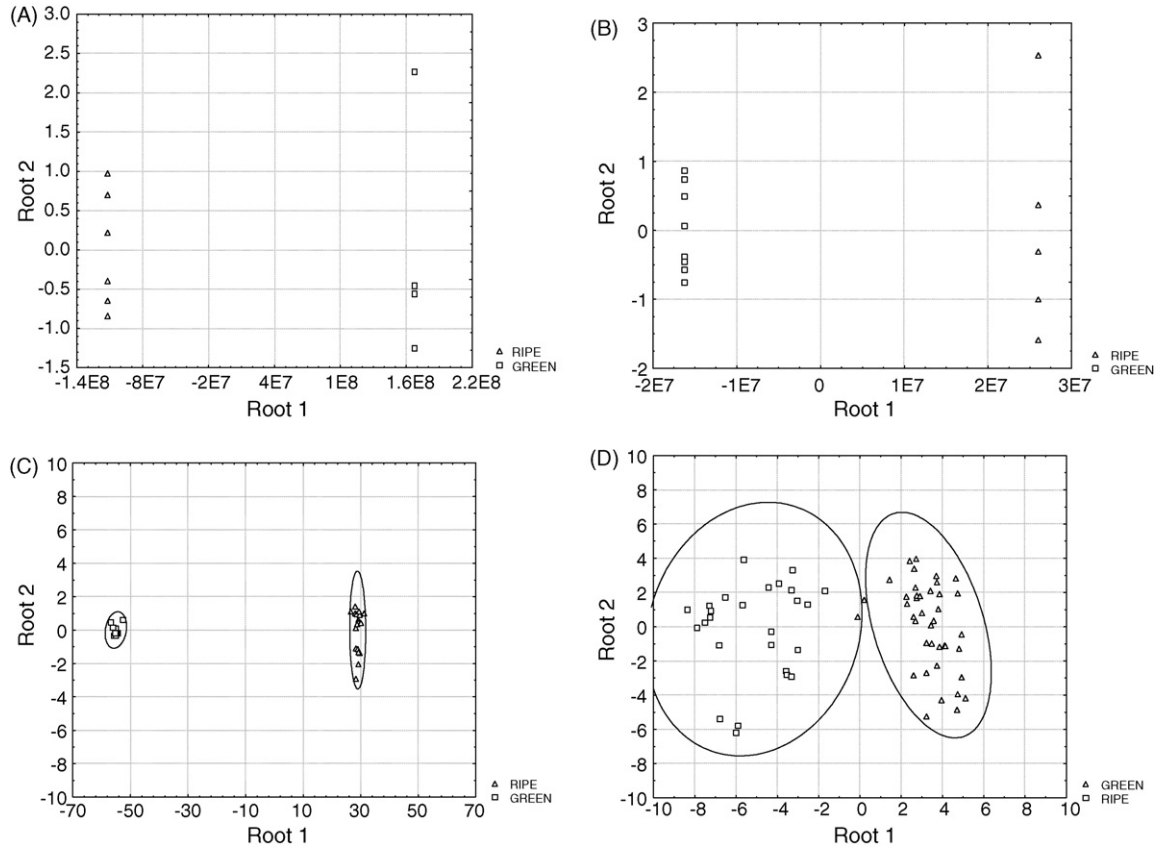

Fig. 2. Comparison between green and ripe 'Cogshall' mangoes by GC using discriminant factor analysis of homogenate for fruit harvested (A) 61 d, (B) 75 d, (C) 103 d, and (D) 115 d passed flowering, immediately after harvest (green), and after 1 week of ripening (ripe).

3.1.2. Comparison of mango harvest maturities within a ripening stage

For green 'Cogshall' fruit, pH generally increased with increasing harvest maturity, but for ripe fruit, there were no differences between harvest dates (Table 2). For TA, there were no significant differences between harvest dates for either green or ripe fruit. TSS was higher for green fruit harvested at 103 d, and higher for ripe fruit harvested at 103 and 115 d. This indicates that the fruit were sweeter when harvested later.

3.2. Volatiles

3.2.1. Comparison of green and ripe fruit

Both enose and GC were able to separate 'Cogshall' and 'Keitt' mangoes by ripeness stage at all harvest maturities tested due to volatile differences. Analysis by both enose (Fig. 1 A–D) and GC (Fig. 2 A–D) using DFA showed a clear separation between fruit right after harvest (green) and after ripening (ripe) for 'Cogshall' fruit homogenate samples from each harvest. The enose also separated intact green and ripe 'Keitt' mango fruit harvested at the full sized mature green stage (Fig. 1E). Data obtained by GC showed better separation than those obtained by enose, as indicated by the much larger scale (over 1 million fold lager for GC data) on the *X*-axis (Root 1) of the discriminant analysis for mangoes harvested 61 and 75 d past flowering (Fig. 2A–C). Separation of mangoes harvested 115 d past flowering using GC (Fig. 2D) was not as good as separation using enose (Fig. 1D). Confidence ellipses for Fig. 2A and B were not drawn because the separation was so wide that they would appear as strait lines through the overlapping data points.

To understand the enose and GC separations by DFA (Figs. 1 and 2) as well as the effect of ripening on the mango volatile profile, individual volatiles were analyzed by GC using volatile peak areas (Table 3). The analysis of volatiles by GC showed that the fruit harvested earlier (61 and 75 d) tended to produce more volatiles right after harvest (green fruit) compared to ripened fruit (except for 3-carene, γ-terpinene and α-terpinolene), but without being significant except for hexanal, octanal (75 d), and *cis*-3-hexenol (Table 3, significance between "green" and "ripe" indicated by a "(*)" for each harvest day). As harvest maturity advanced (103 and 115 d), ripened fruit exhibited higher levels of most volatiles, significant for α- and β-pinene, limonene, γ-terpinene, α-terpinolene, β-caryophyllene and α-hmulene for 115 d fruit; and 3-carene, myrcene and α-terpinene for 103 and 115 d fruit. Hexanal, octanal and *cis*-3-hexenol remained significantly higher in green fruit, however. Total volatiles were always higher in ripe versus green 'Cogshall' fruit due mostly to δ-3-carene and, to a lesser extent, α-terpinolene. Bender et al. (2000) found that tree ripe mangoes exhibited higher levels of all volatiles measured except hexanal than did mangoes harvested mature green.

Table 3
Differences of volatile production (by dynamic headspace analysis) between harvest dates for homogenate of green 'Cogshall' mango fruit (sampled after harvest) and fruit ripened for 1 week at room temperature (ripe)[a]

Volatiles	Relative peak area (×1000 mV)							
	Green				Ripe			
	61 d	75 d	103 d	115 d	61 d	75 d	103 d	115 d
Ethanol	195 a	68 b	59 b	97 b	171 NS	146 NS	73 NS	139 NS
α-Pinene	995 a	380 b	177 b	288*** b	699 A	420 AB	282 B	585*** A
Toluene	547 a	224 b	129 b	225 b	535 NS	278 NS	222 NS	395 NS
β-Pinene	133 a	47 b	30 b	40* b	89 NS	45 NS	36 NS	75* NS
Hexanal	816* b	648*** b	1,740** a	1,990*** a	481* AB	252*** B	453** B	750*** A
3-Carene	32,940 ns	42,088 ns	18,980* ns	35,119* ns	80,372 A	43,063 AB	35,361* B	68,044* AB
Myrcene	2,579 a	853 b	332* b	817* b	2,288 A	1,078 B	843* B	1,668* AB
α-Terpinene	322 a	182 ab	97* b	154** b	560 A	223 B	206* B	395** AB
Limonene	3,885 a	1,418 b	632 b	1,209* b	2,802 A	1,355 B	1,071 B	2,040* AB
γ-Terpinene	807 a	494 ab	199 b	390* b	1,065 A	499 B	338 B	658* AB
cis-3-Hexenal	115 a	50 b	65 b	89 ab	146 NS	62 NS	72 NS	114 NS
o-Cymene	1,879 a	556 b	292 b	512 b	1,135 NS	566 NS	443 NS	760 NS
p-Cymene	1,316 a	460 b	275 b	453 b	1,166 NS	603 NS	458 NS	798 NS
Unknown	758 a	311 b	161 b	282* b	739 A	339 B	289 B	542* AB
α-Terpinolene	2,634 a	1,508 ab	740* b	1,263* ab	3,958 A	1,724 B	1,482* B	2,815* AB
Octanal	101 ns	81*** ns	103* ns	107*** ns	62 NS	26*** NS	52* NS	50*** NS
Heptenal	1,103 a	366 b	272 b	561 ab	745 NS	441 NS	341 NS	631 NS
cis-3-Hexenol	431*** a	276*** bc	194* c	362*** ab	82*** AB	22*** B	74* AB	122*** A
Unknown	380 a	137 b	85 b	146 b	333 NS	176 NS	137 NS	235 NS
Unknown	534 a	210 b	133 b	209 b	457 NS	228 NS	184 NS	297 NS
Decanal	10 a	6 ab	2 b	1 b	6 NS	6 NS	4 NS	3 NS
α-Copaene	609 a	394 b	227 b	226 b	395 NS	393 NS	270 NS	355 NS
β-Caryophyllene	1,102 a	583 b	302 b	308* b	863 A	650 AB	526 B	510* B
α-Humulene	190 a	105 b	58 b	62* b	147 A	111 AB	84 B	88* B
Total volatiles	55,991	51,439	25,493	44,907	10,7007	52,696	43,294	81,764

[a] For each volatile compound, differences between "green" and "ripe" within a harvest day are indicated with *, **, ***: significant at $P<0.05$, $P<0.01$, and $P<0.001$, respectively. Differences between days after harvest within Green and Ripe fruit are indicated by lower and upper case letters, respectively. Mean separations were performed using the LSD test ($\alpha=0.05$).

3.2.2. Comparison of mango harvest maturities within a ripening stage

The enose and GC were somewhat successful in separating 'Cogshall' fruit, based on their volatile profile, from the different harvest maturities determined by days passed flowering. Homogenate of green 'Cogshall' mangoes, harvested 115 d after fruit set (most mature at harvest), were separated from those harvested earlier by the enose (Fig. 3A). Green 'Cogshall' mangoes harvested 103 d after fruit set (the next most mature) had some overlap, but were mostly separated from those fruit harvested at 61 and 75 d after fruit set, which did not separate from each other. After ripening, the fruit harvested at 115 and 103 d after fruit set separated from each other and from the fruit harvested earlier (Fig. 3B). Fruit harvested at 75 and 61 d did not separate from each other. Again, the GC showed better separation of green 'Cogshall' fruit homogenate based on harvest matu-

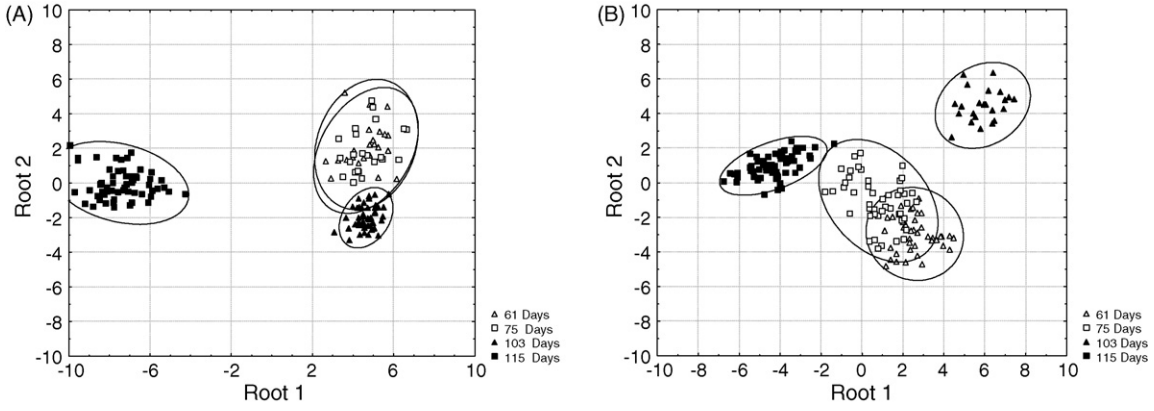

Fig. 3. Comparison between harvest dates by enose using discriminant factor analysis of 'Cogshall' mango homogenate (A) for fruit harvested 61, 75, 103 and 115 d after flowering, immediately after harvest (green) and (B) after 1 week of ripening (ripe).

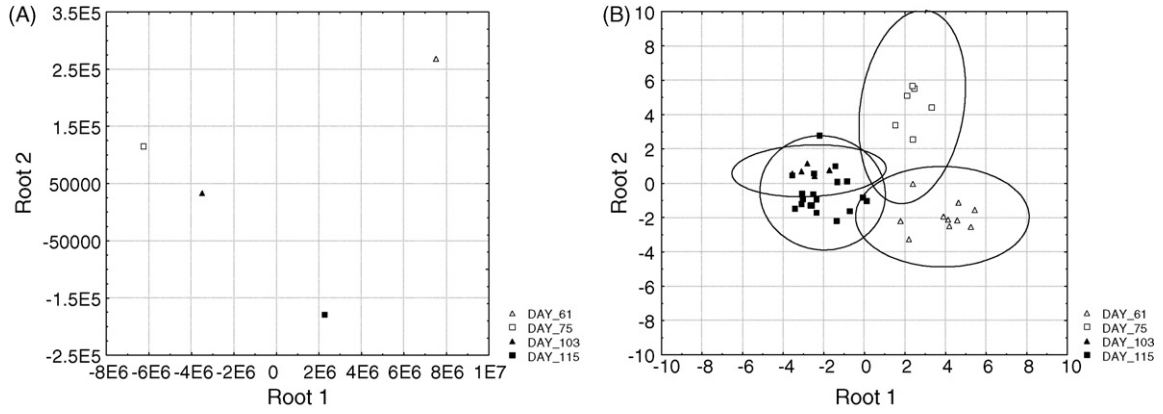

Fig. 4. Comparison between harvest dates by GC using discriminant factor analysis of 'Cogshall' mango homogenate (A) for fruit harvested 61, 75, 103 and 115 d after flowering, immediately after harvest (green) and (B) after 1 week of ripening (ripe).

rity (Fig. 4A, confidence ellipses are too small to see and data points overlap and appear as single points due to large scale on *X*-axis) than did the enose; however, this was not the case for ripe fruit (Fig. 4B). Fruit harvested 115 and 103 d after flowering were not separated while the earlier-harvested fruit (75 and 61 d after fruit set) showed some separation, nevertheless, all groups showed some overlap.

Analysis of individual volatiles by GC was again performed to understand the separation of fruit using DFA and the effect of harvest maturity. The GC analysis showed that, there were generally higher volatiles in green and ripened fruit from the earliest harvest (61 d), compared to fruit from later harvests, with the exception of hexanal (for green and ripe) and *cis*-3-hexenol (for ripe fruit) (Table 3). There are less significant differences after ripening, however. It appears that the terpenoid volatiles decrease the longer the fruit stay on the tree through 103 d past flowering, but their concentrations pick up again in the most mature fruit, harvested at 115 d. It has been reported that

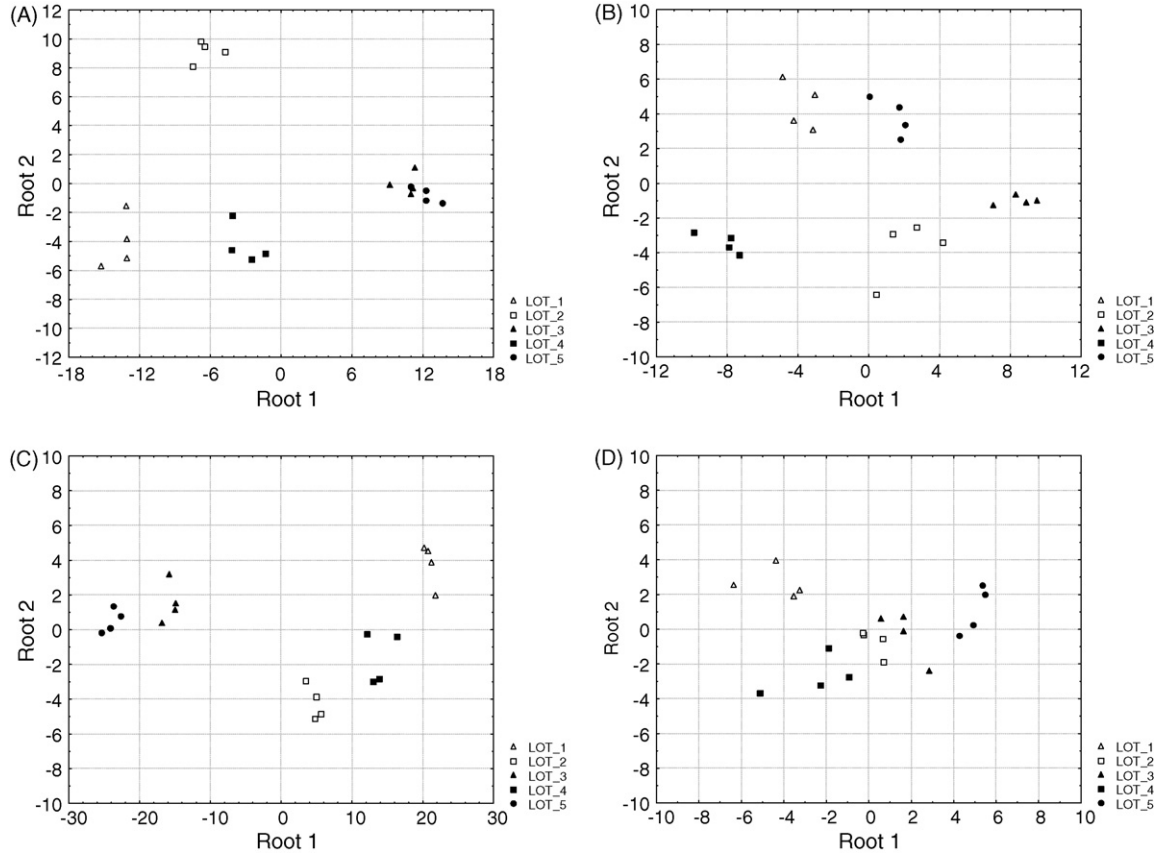

Fig. 5. Enose separation using discriminant factor analysis of intact 'Kent' mangoes harvested at different sizes, representing different maturities (mean weight in g: lot 1, 894; lot 2, 743; lot 3, 469; lot 4, 385; lot 5, 276), (A) day after harvest (green) and (B) after 1 week of ripening (ripe); and intact 'Keitt' mangoes harvested at different sizes (mean weight in g: lot 1, 1563; lot 2, 1194; lot 3, 688; lot 4, 528; lot 5, 364), (C) day after harvest (green) and (D) after 1 week of ripening (ripe).

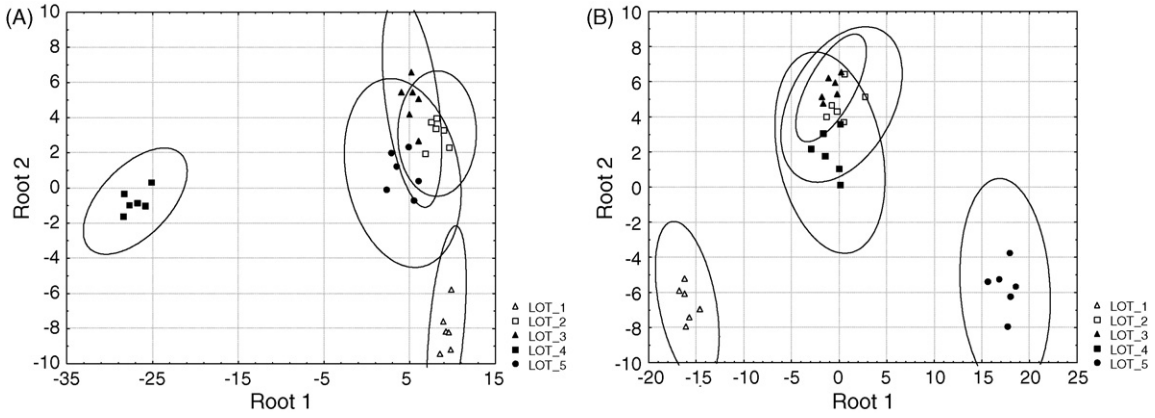

Fig. 6. GC separation using discriminant factor analysis of (A) 'Kent' homogenate of fruit harvested at different sizes (mean weight in g: lot 1, 894; lot 2, 743; lot 3, 469; lot 4, 385; lot 5, 276) after 1 week of ripening, and (B) 'Keitt' homogenate of fruit harvested at different sizes (mean weight in g: lot 1, 1563; lot 2, 1194; lot 3, 688; lot 4, 528; lot 5, 364) after 1 week of ripening.

most of the glycosidically bound aroma compounds increased in mango pulp as maturity progressed, which included terpenes (Lalel et al., 2003a) and that harvest maturity affected levels of aroma volatiles where fruit harvested less ripe had higher levels of monoterpenes and sesquiterpenes compared to fruit harvested ripe which had higher levels of esters, alkanes and nor-isoprenoids (Lalel et al., 2003b).

For non-destructive analysis of intact Florida mangoes, the enose separated 'Kent' green, except lots 3 and 5 (Fig. 5A) and ripe (Fig. 5B) fruit by maturity (as indicated by fruit size) as well as 'Keitt' green fruit (Fig. 5C) using DFA, but there was poor separation of 'Keitt' ripe fruit for lots 2 and 3 (Fig. 5D). Due to the relatively small number of samples, meaningful confidence ellipses were not obtained. Unfortunately, headspace samples from the containers of intact fruit did not yield enough volatiles to be detected by GC, therefore, the fruit were homogenized after ripening and volatiles from ripened 'Kent' and 'Keitt' fruit homogenates from the various lots were analyzed by GC using DFA. The data showed that fruit homogenate from lots 4 or 5 (smallest fruit) and lot 1 (biggest fruit) was generally separated from the other lots (Fig. 6A and B for 'Kent' and 'Keitt', respectively).

Since it appeared that there were volatile differences based on peak heights for the "Cogshall' fruit, some important mango volatiles were quantified for the 'Kent' and 'Keitt' homogenates. For 'Keitt', lot 5 was shown to be higher in 3-carene, myrcene, limonene compared to the other lots (Table 4A), while for 'Kent', Lot 4 was higher in most volatiles (Table 4B), and especially for acetaldehyde, acetone, ethanol, β-pinene, 3-carene, myrcene, limonene, and α-terpinolene. Therefore, the analysis by GC helped explain the results obtained by the enose, and were consistent with those found for the 'Cogshall' fruit and those found by Lalel et al. (2003b) where fruit harvested less ripe tended to have higher levels of monoterpenes and sesquiterpenes compared to fruit harvested ripe.

3.2.3. *Comparison of mango varieties*

To determine if mango varieties could be separated based on volatiles, ripe 'Kent' and 'Keitt' fruit were compared by enose and GC with DFA. Separation of ripe 'Kent' and 'Keitt'

Table 4
Static headspace of 'Keitt' and 'Kent' mango homogenate from different size classes (lots 1–5 separated by g fresh weight) after ripening

	Acetald	Acet	Meth	Eth	α-Pin	β-Pin	3-Car	Myr	Lim	*p*-Cym	α-Terp	α-Cop	Cary
(A) Keitt size class[a]													
Lot 1	5.47 ab	0.20	115.62	15.31	2.16	0.09	9.26 b	0.50 b	0.36 b	0.01	0.91	0.00	0.00
Lot 2	3.65 c	0.18	108.33	11.90	2.16	0.05	10.52 b	0.59 b	0.37 b	0.00	0.92	0.00	0.17
Lot 3	5.52 a	0.20	109.78	13.01	1.44	0.09	9.76 b	0.60 b	0.36 b	0.01	0.62	0.02	0.17
Lot 4	4.42 bc	0.20	111.05	13.71	2.16	0.14	11.06 b	0.60 b	0.37 b	0.01	0.94	0.00	0.34
Lot 5	5.70 a	0.20	108.71	14.95	2.19	0.14	15.47 a	0.94 a	0.43 a	0.01	1.02	0.02	0.51
(B) Kent size class[b]													
Lot 1	12.00 b	0.25 bc	115.13	20.41 b	2.16 b	0.05 b	9.29 b	0.56 b	0.36 b	0.00 c	0.91 b	0.02	0.17
Lot 2	9.90 c	0.22 c	111.12	5.01 b	2.15 b	0.00 b	9.04 b	0.51 b	0.35 b	0.00 bc	0.90 b	0.00	0.00
Lot 3	9.08 c	0.22 c	111.25	12.66 b	2.16 b	0.05 b	10.36 b	0.59 b	0.36 b	0.01 ab	0.92 b	0.00	0.00
Lot 4	43.94 a	0.43 a	109.57	59.17 a	2.17 a	0.14 a	13.29 a	0.80 a	0.40 a	0.01 a	0.97 a	0.00	0.34
Lot 5	12.74 b	0.26 b	113.95	16.41 b	2.16 b	0.00 b	10.84 ab	0.66 ab	0.38 ab	0.01 a	0.93 b	0.00	0.00

Data (μL/L) are means of three replications (Acetald, acetaldehyde; Acet, acetone; Meth, methanol; Eth, ethanol; α-Pin, α-Pinene; β-Pin, β-Pinene; 3-Car, 3-carene; Myr, myrcene; Lim, limonene; *p*-Cym, *p*-Cymene; α-Terp, α-Terpene; α-Cop, α-Copaene; Cary, caryophyllene) [Data are means of three replicates and mean followed by the same letters within a column are not statistically different using the LSD test ($\alpha = 0.05$).].

[a] Keitt lot 1 = 1563 ± 265 g; lot 2 = 1194 ± 172; lot 3 = 688 ± 95; lot 4 = 528 ± 51; lot 5 = 364 ± 56.

[b] Kent lot 1 = 894 ± 98 g; lot 2 = 743 ± 70; lot 3 = 469 ± 44; lot 4 = 385 ± 36; lot 5 = 276 ± 42.

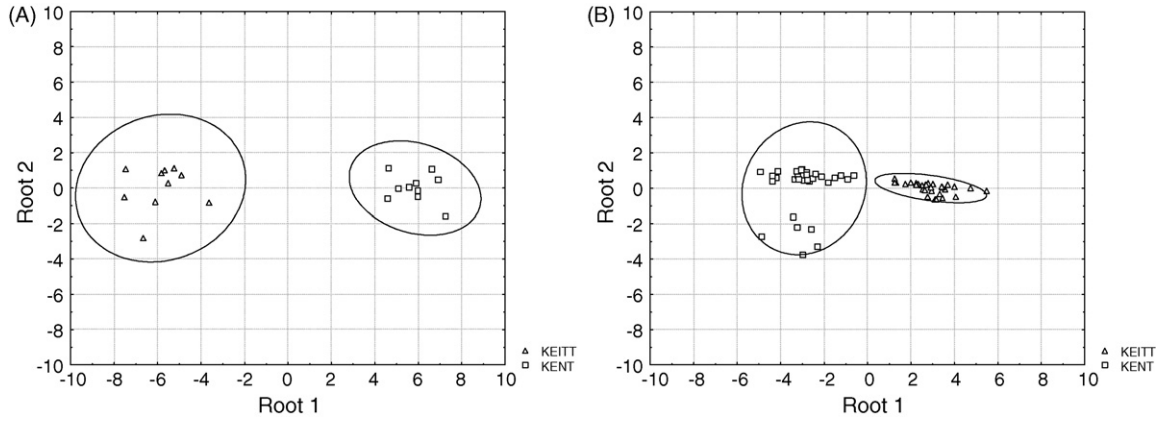

Fig. 7. Separation of intact ripe 'Kent' and 'Keitt' mangoes by (A) enose and (B) GC.

homogenates were achieved by both enose and GC (Fig. 7A and B for enose and GC, respectively), showing that either enose or GC could be used to distinguish mango varieties, and that the varieties, therefore, differed due to their volatile components.

4. Conclusion

One of the objectives of this study was to see if harvest maturity could be discriminated using volatiles that could be detected by enose or GC, in fruit homogenate or, preferably, in whole fruit. This could lead to a possible non-destructive means of determining optimal mango harvest maturity on the tree or in harvested fruit as a predictor of quality. The second objective was to determine the effect of harvest maturity on mango flavor quality factors. It is reported that mangoes harvested at less than ideal maturity result in ripened fruit of less than optimum quality (Narain et al., 1998; Medlicott et al., 1988) based on sugar acid ratios. In this study, later harvests resulted in increased quality in terms of higher solids and lower acids than in fruit from the earlier harvest maturities (Table 2) as has been shown before (Narain et al., 1998; Medlicott and Thompson, 1985). Later-harvested fruit also had different volatile profiles (less terpenes) than earlier-harvested fruit (Tables 3 and 4) upon ripening, which would affect flavor quality. The enose and GC were able to separate ripe from green 'Cogshall' fruit homogenate at each harvest maturity, and separate all harvest maturities for green fruit homogenate (immediately after harvest), and to a lesser extent ripened fruit homogenate by separating the two later (103 and 115 d past flowering) from the two earlier (61 and 75 d past flowering) harvest maturities for 'Cogshall' fruit.

For intact fruit, based on size, the enose was able to generally separate the different size classes for both green and ripe fruit for intact 'Kent' and 'Keitt' mangoes, with some overlap for green 'Kent' of lots 3 and 5, and of ripe 'Keitt' lots 2 and 3. While size is a crude indicator of mango harvest maturity compared to days past flowering, it was interesting to note that the classification was somewhat successful. This demonstrates the benefit that could be obtained if a hand-held enose device were developed that could determine optimal harvest maturity for mangoes on the tree by the volatiles emitted, or an enose device that could be used as a screening tool on fruit after harvest.

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